

Joining Carbon-Carbon Composites and High-Temperature Materials with High Energy Electron Beams

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PROGRESS REPORT

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Progress Report

This report is submitted to describe progress in High Energy Electron Beam (HEEB) joining experiments during the third and fourth quarter of 1997. This report is submitted to fulfill the Contract Data Requirements List requirements for progress reports.

Executive Summary

- Program Goals Addressed During This Period.

Experimental work was directed at formation of a low-stress bond between carbon-carbon and aluminum, with the objective of minimizing the heating of the aluminum substrate, thereby minimizing stresses resulting from the coefficient of thermal expansion (CTE) difference between the aluminum and carbon-carbon. A second objective was to form a bond between carbon-carbon and aluminum with good thermal conductivity for electronic thermal management (SEM-E) application.

- Substrates & Joining Materials Selected During This Period

Carbon-Carbon Composite (CCC) to Aluminum
CCC (Cu coated) to Aluminum
Soldering Compounds based on Sn/Pb and Sn/Ag/Cu/Bi compositions

- Soldering Experiments Performed
 - Conventional Techniques
 - High Energy Electron Beam (HEEB) Process

Experimental Progress - Electron Beam Joining

The Phase II program focuses on three applications for joining CC composites.

- Electronic Thermal Management
 - Standard Electronic Module (SEM-E)
- Spacecraft Thermal Management
 - Large Dimensionally-Stable Structures (LDSS)
- High Temperature Structures
 - Reusable Launch Vehicle (RLV)

Joining experiments using conventional soldering techniques and electron beam soldering were conducted during the third and fourth quarters of 1997. Electron beam experiments were performed using the SRL 1.5 MeV linear induction accelerator. These experiments are described in Section 2 following a review of the background and motivation for conducting soldering experiments to join CCC's to aluminum for electronic thermal management. Plans for the final phase of this project are described in Section 3.

1. Background and Motivation

High energy electron beam (HEEB) brazing is a process for joining low coefficient of thermal expansion (CTE) materials such as carbon-carbon (CC) composites, C/CSiC composites or diamond to higher CTE substrates or to themselves at high temperatures ($> 450^{\circ}\text{C}$). Brazing is the joining of metals (or metal-coated substrates) through the use of heat and a filler metal - one whose melting temperature is above 840°F (450°C) but below the melting point of the metals being joined.¹

Table 1.1 shows the materials joined under programs at SRL, the brazing alloys used and the CTE ratios of those materials. Computer simulations, which were discussed in an earlier report, showed that when the ratio of metal substrate CTE to carbon CTE is in the range of 1-3, HEEB joining can completely eliminate the braze stresses. For a CTE ratio above 4, such as CC to aluminum, the stresses can be reduced but not eliminated. For CC to aluminum, the computer simulations showed that the maximum reduction using HEEB brazing is approximately a factor of four times compared to conventional vacuum-oven brazing. Unfortunately, this is insufficient to reduce the braze stresses below the CC's interlaminar strength. The result is low-strength joints with reduced percentage area bonding.

Table 1.1 Materials Used in HEEB Brazing

Materials Joined	Braze Alloy	Substrate CTE ($\times 10^{-6}$ in/in)	CTE Ratio	Notes
CC to CC or C/SiC	CuSiI, MoSi2	0-2	1	High Temp Applications
CC to Aluminum	Al/Si	17	8	Electronic Heat Sinks
Thermally Stable Diamond to WC/Co	CuSiI	6	3	Oil and Gas Drilling Applications*

* Reference 2

Based on suggestions from Craig Ohlhorst, NASA technical monitor, and, after giving further consideration to the computer simulations and experimental results for brazing CC to aluminum and the requirements for electronic heat sinks, we decided to focus our current efforts on lower-temperature joining processes. This is reasonable because electronic modules would not operate at temperatures which require joining materials using braze alloys ($> 450^{\circ}\text{C}$). The main advantages of using CCC's in electronic modules is to reduce the weight of the assembly and heat stress on the electronic components through the high thermal conductivity of the carbon. The joints must also have good thermal conductivity, similar to carbon, and have mechanical properties similar to the interlaminar shear strength of the CCC.

There are three possible ways to join CCC's to aluminum and achieve high strength joints with good thermal conductivity and thermal stability (to 450°C) using HEEB processing:

- 1) High-temperature thermosets (adhesives) such as epoxies and cyanate esters;
- 2) High temperature thermoplastic polymers such as polyimides or polyetherether ketone (PEEK)
- 3) Soldering.

A quick survey of thermoset adhesives indicated that, although they might provide sufficient mechanical strength from ambient to 200°C , mechanical properties would be inadequate for long duration (> 24 hr) especially at temperatures $> 200^{\circ}\text{C}$. More importantly, the thermal conductivity of the best adhesives is at least an order of magnitude below the CCC and aluminum substrates. **Table 1.2** is a list of relevant properties of adhesives surveyed for this application. Information in **Table 1.2** was obtained from company literature. While these adhesives may not be suitable for the high temperature applications, the properties of this class of bonding agents may need to be considered for lower temperature requirements.

Table 1.2 Thermally Conductive Adhesives

company	Adhesive	CTE /°C ppm	Thermal Conductivity W/m °C	Lap Shear Strength psi substrate/substrate	Cure Conditions
IPN Industries	EGA 439	NA	2.0	2400 Al-Al	72 hr/RT
Loctite Corp	Output 383	710	0.50	1500 Al-Epoxy GI	72 hr/RT
Resin Technology	Oxy-Bond 153	26	1.4		24 hr/RT
Norlabs	Si 923	13 est*	0.65	595 tensile str**	7 days/RT
3M	Silicone	400	0.43	70	Min/RT
Polycast	Epoxy 287		4.2		
Polycast	Si RTV893		1.4		
Bryte Tech	Epoxy		~5 W/mK	1000	1 hr/250°F
Bryte Tech	Cyanate Ester		10-12		180 min 250 °F

*estimated value based on company data **tensile strength

The second approach, high temperature thermoplastic polymers as adhesives, has the same limitation in thermoconductivity as do organic thermosets. Furthermore, little is known about using thermoplastics as hot-melt adhesives to join carbon-carbon to aluminum. While this approach may not be feasible for current requirements in electronic modules, EB processing using high-temperature thermoplastics may be worth consideration for other NASA programs.

The third approach, soldering, offers better potential for developing joints with good thermal, electrical conductivity and mechanical strength over the desired temperature range (ambient to 450 °C) for electronic applications. Soldering is the joining of metals (or metal-coated substrates) through the use of heat and a filler metal at a temperature ≤ 450 °C.¹

For most electronic applications, the upper service temperature would be approximately 150 °C; thus, the CTE mismatch between aluminum and carbon would be less of a factor, resulting in lower residual stresses in the soldered joints. Soldering is a well-established and widely-used process for joining metals. A wide variety of soldering compositions are available at a relatively low cost. Different methods are available to join metals, including flame or torch soldering, furnace soldering, and soldering irons. Very little is known about using HEEB to solder materials. An additional challenge would be to develop soldering compositions to join carbon to itself or to aluminum. It was felt, however, that HEEB could be used to produce high-strength solder joints with low residual stresses between carbon and aluminum.

2. Experimental Program

2.1 Carbon-Carbon Composite (CCC) to Aluminum

Essentially no information exists on soldering graphite or other carbon materials. Carbon and graphite can be joined using brazing techniques where the carbon surface is precoated with either a metallic or intermetallic layer so that brazing can be accomplished with a conventional filler material.³ For example, chemical vapor deposition (CVD) can be used to precoat the carbon with molybdenum or tungsten; this is often accompanied by carbide formation which strengthens the bond between the carbon and the metal layer. However, for reasons mentioned at the beginning of this report, a brazing process was unacceptable, and molybdenum or tungsten cannot be soldered directly (see section below on copper coatings).

Aluminum forms a tenacious oxide layer upon exposure to air and is therefore difficult to solder, but it is still solderable. Special liquids (acid fluxes) have been developed by industry to facilitate soldering of aluminum. The same generalizations hold for the brazing of aluminum, except that the braze temperatures are much closer to the solidus temperature of aluminum and its alloys, and thus closer temperature control is required to braze aluminum.⁴

2.2 CCC (Ti coated) to Aluminum

Previous work under this contract⁵ had demonstrated that titanium-coated CCC could be joined to a tin-coated aluminum substrate using an aluminum-silicon eutectic braze alloy (88 Al/12 Si) in a HEEB process. The estimated joining temperature for this experiment was 625 °C, which is between the melting point of aluminum (660 °C) and the solidus temperature of the braze (577 °C). The surface temperature of the CCC was estimated > 1000 °C. While the temperature of the aluminum substrate was estimated at < 577 °C, it was too high to minimize residual stresses from the brazing experiment. It also required extremely good process control to heat the braze alloy to the correct temperature range without melting the aluminum substrate. Thus, a lower temperature joining process (soldering) is still needed for this application.

During the last reporting period, a brief survey of the literature on metallurgical joining methods and metal phase transition diagrams, plus discussions with several suppliers of soldering materials, indicated that there were unlikely to be any low temperature alloys that would wet titanium or similar metals. Thus, the approach of using Ti-coated substrates to achieve this objective was discontinued at this point in the search for more suitable metal coatings for carbon.

2.3 Copper-Coated CCC to Aluminum

Previous workers had shown that CCC's could be coated with copper to facilitate joining to copper metal plates. The carbon/carbon composite is first coated with a refractory metal and then followed by a copper layer suitable for bonding.^{6,7} The carbon-carbon composite used in this study along with some properties⁸ is listed in **Table 2.1**.

Table 2.1: Carbon-Carbon Composite used in Phase II Joining Experiments

Material	Description	CTE / °F ppm		Thermal Conductivity W/mK, 3000 °F	
ACC4 Carbon-Carbon Advanced Technologies Ft. Worth, TX	Eight harness satin weave 2-D material, T-300 fibers Woven prepreg, Phenolic resin-based matrix	Warp	0.5	Warp	36
		Fill	0.5	Fill	36
		Across ply	3.5	Across ply	5

During this period, carbon/carbon composite plates (0.072 “ average thickness) were copper coated according to the process described above and soldered using various soldering compositions. Copper-coated aluminum, 6061 T6 alloy, (Cambridge Plating, Belmont, MA) was the aluminum substrate.

Soldering materials were obtained from several suppliers (**Table 2.2**). Included in the table are solid wire solders, acid-core, and rosin-core solders. Physical property data were obtained from manufacturer’s data sheets. Solid wire solders were used in conjunction with recommended fluxes. Physical properties for various elements or metal alloys used in this study are given in **Table 2.3**. The data were obtained from standard references.^{1,9}

2.4 Conventional Soldering Experiments

Prior to HEEB joining, soldering experiments were performed using conventional procedures: torch soldering, soldering iron in conjunction with a hot plate, furnace soldering. The latter technique was done both in air and under vacuum without any noticeable difference. While torch soldering appeared to be acceptable, use of a soldering iron gave more uniform joints.

Initial attempts to furnace solder the composite to aluminum using a flat piece of solder foil were unsuccessful, probably, because insufficient time was allowed for the solder to wet the individual surfaces prior to bonding. In subsequent trials, each piece of composite and aluminum were pretreated (tinned) with the appropriate solder/flux combination by carefully heating the desired sections with the soldering iron (in conjunction with a hot plate if necessary for the higher temperature solders). The soldering iron was the most effective way to obtain a uniform solder coating thickness of 5 - 10 mil.

The pretinned pieces were then joined first using a soldering iron and then in the furnace for approximately 15 minutes at 50 °C higher than the liquidus temperature of the solder. Once an acceptable solder joint was obtained for a given composition with the soldering iron/furnace processes, the composition was soldered with the EB with various time-temperature conditions (**Table 2.4**, next section).

Table 2.2 Solder Compositions and Physical Properties

Solder	Composition	melting range °C	Thermal Conductivity, W/m-K	Coefficient of Thermal Expansion, CTE, $\mu\text{-in/in K}$
Kester 40/60 Rosin Core	Sn 40/Pb 60	183/238	44*	25
Eutecrod 157	Ag 5%/Sn 95%	218/221	69	12
Oatey SafeFlo Lead-Free	Sn >90/Cu <5 Bi <5/Ag < 5	216/235	77*	
Multicore Rosin Core	HMP Solder 93.5 Pb/5 Sn/1.5 Ag	296/301	43*	

*Estimated Values, based on components.

Table 2.3 Physical Properties of Elements and Metal Alloys

Element or Metal Alloy	Composition	Melting Pt or Liquidus/Solidus °C	Thermal Conductivity, W/m-K	Coefficient of Thermal Expansion CTE, μ -in/in K
Aluminum	100 Al	660	237	23.3
Aluminum	6061 T6 alloy	582-652	167	23.6
Bismuth	100 Bi	271	7.9	13.3
Carbon		3727	24	
Carbon	diamond		> 1000	1
	graphite		5.7	26.7
	graphite		2000	-1.22
Copper	100 Cu	1083	401	16.4
Gold	100 Ag	1063	317	14
Indium	100 In	156	82	33
Lead	100 Pb	327	35	29.3
Nickel	100 Ni	1453	91	13.3
Silicon	100 Si	1410	150	2.8 - 7.3
Silver	100 Ag	960	429	18.9
Tin	100 Sn	232	67	19.9
Titanium	100 Ti	1668	22	8.5
Tungsten	100 W	3387	174	4.6
Zinc	100 Zn	420	116	39.7
Tin-lead	60 Sn/40 Pb		50	
Tungsten-copper	50 W/50 Cu		90	
Silver-copper	50 Ag/50 Cu		310	
Silver-lead	95 Ag/5 Pb		220	
	50 Ag / 50Pb		35	
Silver-zinc-copper	26 Ag/70 Zn/4 Cu		170	
Indium-tin	52 In/48 Sn	118 eutectic	34	20
Indium-silver	97 In/3 Ag	143 eutectic	73	22
Tin-lead-indium	70 Sn/18 Pb/12 In	154/167	45	24
Indium-lead	70 In/30 Pb	165/175	38	28

2.5 HEEB Soldering Experiments with Cu-Coated Al

Two different solder joints were prepared during this period: The first geometry was a lap joint to measure shear strength by tensile loading (ASTM D 1002), and the second type of specimen was a 1-in² laminate for thermal conductivity measurements. For all the EB experiments, the CCC specimen was placed on top of the Al substrate, which was then attached to a water-cooled target in a vacuum chamber. The high energy electron beam (HEEB) processing system used in this study is shown in **Figure 1**. Surface temperatures were measured with an infrared pyrometer.

The EB experiments were conducted by an off sample-on sample process, which produces rapid heating and temperature rise on the surface of the carbon. In this procedure, the HEEB pulse rate was first increased to a desired off the sample, and then shifted onto the sample for a fixed amount of time. During the last reporting period we used frequencies of, for example, 200 Hz for 3 sec (**Figure 2**).

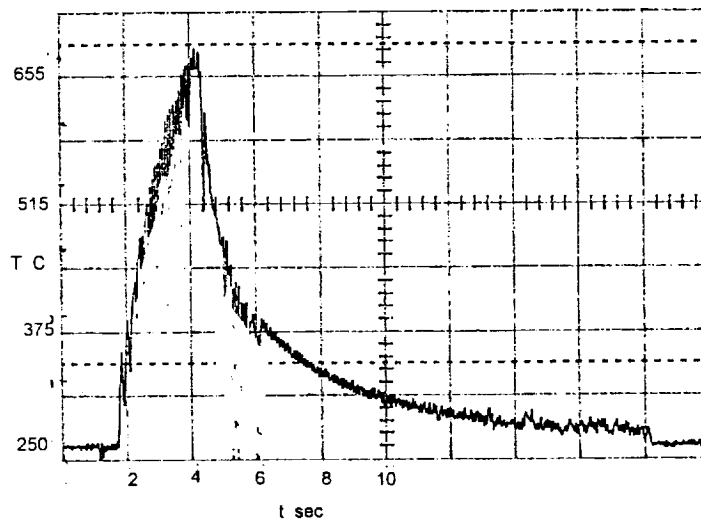


Figure 2. Off Sample – On Sample: 200 Hz / 3 sec

We are now using higher frequencies for shorter periods (300 – 400 Hz / 0.25 sec). These new conditions are at higher powers than what was used previously. The recorded surface temperatures in the latest experiments were at least 200 °C above the liquidus temperatures of the solder for a fraction of a second. This should insure that the solder interface fully melted. The HEEB process volumetrically heats the CCC without heating the bulk of the aluminum substrate; this procedure should reduce residual stresses in the solder joint. No distortion or apparent damage of either the carbon or aluminum resulted from these experiments. **Figure 3** shows a typical time-temperature curve for a run at 350 Hz for 0.25 seconds. As the electron beam power is increased, the rate of temperature rise increases, but the cooling time is determined by the conductive heat transfer rate to the water-cooled backing plate.

HEEB Carbon-Carbon Composite Joining

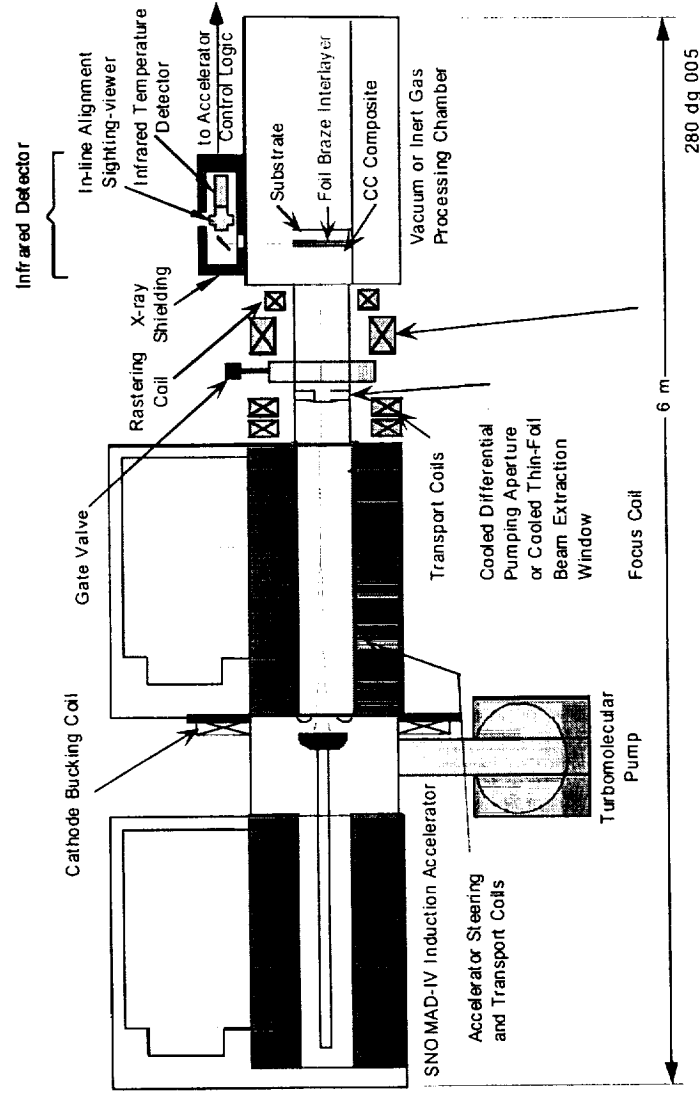


Figure 1. A SNOMAD-IV induction-accelerator-based carbon-carbon composite process system for joining CC to high temperature metallic materials.

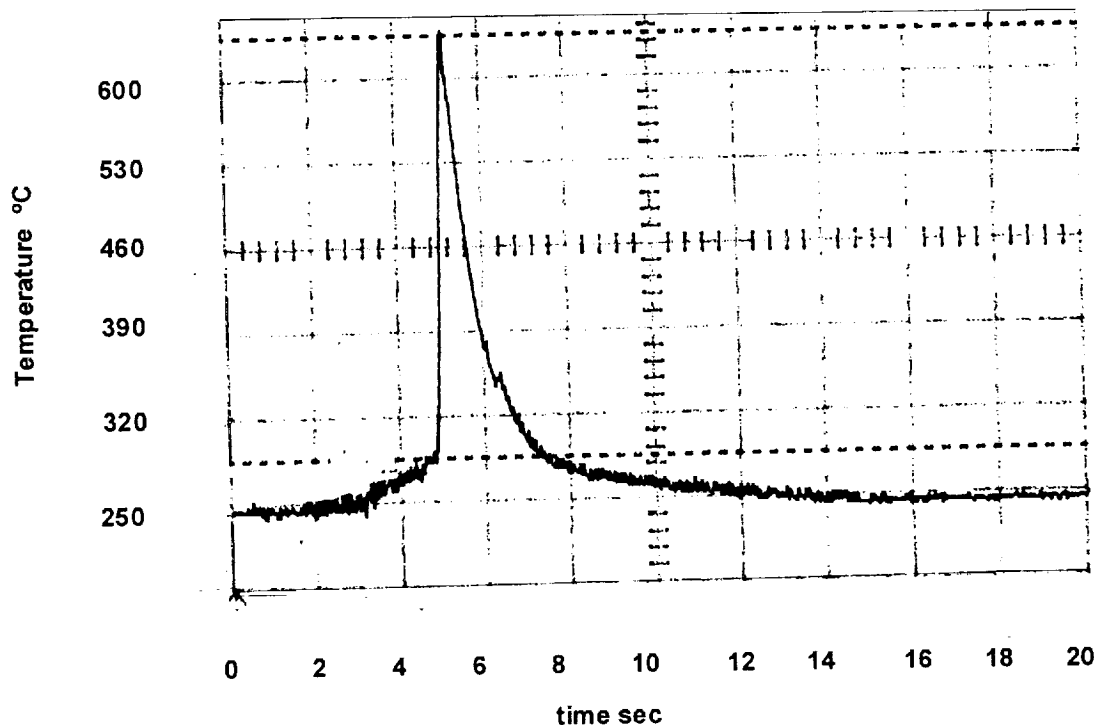


Figure 3. Off Sample-On Sample: Rapid Heating 350 Hz / 0.25 sec.

2.6 Lap-Shear Testing ASTM D 1002

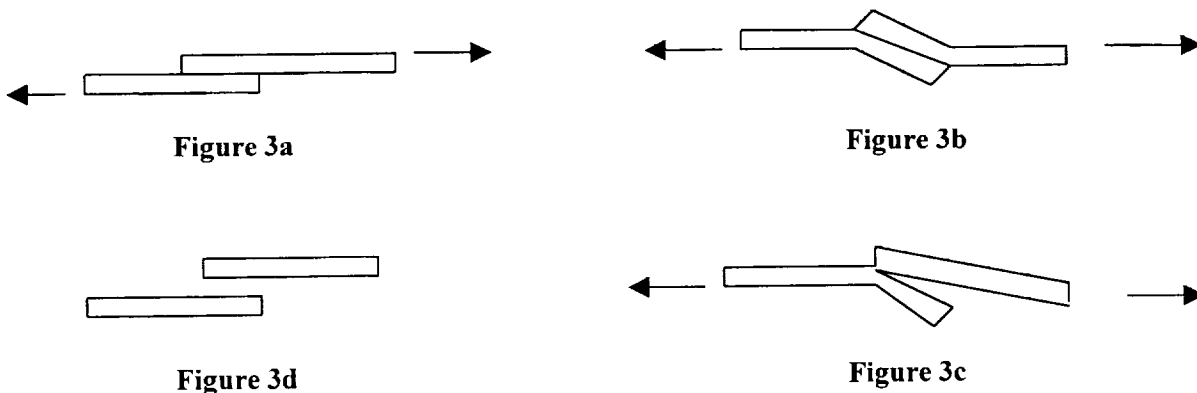
During this reporting period, over 30 samples were prepared by the HEEB process using 4 different solder compositions. Samples which were tested for breaking strength are given in **Table 2.4**. Lap-shear strengths (break strengths) were not as good as those reported during the last period. In most cases, the break strengths were in the range of 89 – 498 psi, with one exception where a value of 835 psi was obtained. During the previous reporting period, break strengths of over 1000 psi were obtained.¹⁰

Table 2.4: Lap-Shear testing of CuAl-CuCC samples bonded using EB processing at surface temperatures between 575-650°C, at 350 pps for 0.2-0.25 seconds.

Solder or Braze	Strength (psi)	Elongation (in)	Comments*
K44 40/60	80-830	0.07-0.13	100% area bonding
Eutecrod	90-350	0.05-0.08	100% area bonding
Oatey SF	80-200	0.03-0.06	100% area bonding
HMP	130-250	0.04-0.13	50% area bonding in some samples

*All samples suffered interlaminar CC-CC failures near the CC/Cu interface. A thin layer (1-10 mil) of carbon remained on the copper surface.

Inspection of the samples showed that the failure mode was primarily interlaminar carbon-carbon separation; a thin layer (ca 1-10 mil) remained on the copper surface. The solder joint remained intact, which indicates that solder failure did not occur. Full area soldering was achieved, except for the HMP solder, which is the highest-melting solder tested. In the present study, the area to be joined was $\sim 1 \text{ in}^2$, which was larger than previously attempted ($\sim 0.25 \text{ in}^2$). Concurrent with delamination (or subsequent to delamination), the exposed copper layer breaks at upper end of the joint. In several cases, the stress-strain test was stopped before the sample fully ruptured, and it was noted that delamination had occurred, but a portion of the copper layer remained intact. These results are consistent with the idea that if a lap-shear joint is heavily stressed (**Figure 3a**), it tends to rotate to line up the forces (**Figure 3b**). In effect, it becomes a peel joint: As the load increases, the joint fails interlaminarly (**Figure 3c**), and then the thin copper layer breaks (**Figure 3d**).



Attempts were made to simulate the failure by manually peeling off the copper layer from a virgin sample of copper-coated carbon. In this case, a thin layer of carbon adheres to the copper layer, but more carbon adhered to the copper in the former case (lap shear specimens). This suggests that the lap-shear specimens undergo primarily interlaminar carbon-carbon failure rather than failure at the carbon-copper interface. The copper layer could be easily polished clean, which suggests that the interfacial strength of carbon to copper is not very high. A fresh carbon surface remains after the copper is removed. Optical microscopy at 80x did not reveal any significant differences between the uncoated and coated carbon surfaces.

Since the solder joint was formed, it is believed that the HEEB irradiation was properly positioned on the targets. Compared to the previous work, higher repetition rates corresponding to higher electron beam power densities were used in the present experiments. The higher powers resulted in peak surface temperatures about 100°C higher than would have been observed with similar input energy at a lower power, due to the balance between electron beam heating and conduction cooling.

The fact that most of the samples fully bonded was determined by inspection of the samples after failure. "Fully bonded" implies that both the upper and lower solder surfaces melted and coalesced to form a solder joint. The exception was the HMP solder, which is the highest melting solder composition used in this study. The upper melting temperature of HMP solder is 301 °C. Since the upper carbon surface temperature recorded for the EB experiments was at least 600 °C, this should have been sufficient to join the surfaces. Inspection of the HMP solder samples revealed that not all of the solder melted; either the EB did not uniformly heat the intended solder joint or the surface temperature measurement is not an accurate indicator of the temperature at the interface. Uniform heating would be especially important for the higher melting solders and braze metals.

The question still remains as to why the present samples are weaker than those reported in the last period. Possibly the higher temperatures weakened the copper-carbon interface. On the other hand, the duration of the present experiments was only a fraction of a second, compared to several seconds previously used. Two additional sets of experiments were run in an attempt to shed light on the failure mechanism. In the first case, samples were soldered using either a soldering iron or an acetylene torch. Results shown in **Table 2.5** indicate that conventional soldering can produce joints equal to or better than the joints prepared by the HEEB process (compare with **Table 2.4** in this report and from the last progress report, reference 5).

Table 2.5 Iron/Torch Soldering and Adhesive Bonding of Cu-Coated CCC to Cu-Coated Aluminum. Lap-Shear Strengths.

Solder or Adhesive	Strength (psi)	Elongation (in)	Comments
K44 40/60	723-1390	0.05-0.15	100% area bonding interlaminar failure
Eutecrod	635-1000	0.05-0.087	Same as above
Oatey SF	990	0.07	Same as above
HMP	825-1260	0.05-0.06	Incomplete Bonding Interlaminar failure

In the second set of experiments, both copper-coated CCC and uncoated CCC specimens were bonded to aluminum and uncoated CCC specimens using a standard structural adhesive, Loctite 334. Electroplated Cu*CCC was also used. The results are shown in **Table 2.6**.

Table 2.6 Lap-Shear Strengths of Adhesive Bonded Specimens Using Loctite 334*

Data Set	Specimen	Strength (psi)	Elongation (in)	Comments
1	Al to Al	> 1000	0.1	Did not break
2	CuAl to CuAl	> 1000	0.1	Did not break
3	CuCCC to CuAl	536-1200	0.09-0.2	Interlaminar failure
4	CuCCC to CCC	758-890	0.12-0.14	Interlaminar failure CuCCC plate
5	CCC to CCC	1098-1364	0.11-0.14	Adhesive Failure
6	Cu [#] CCC to CuAl	327-385	0.09-0.1	[#] electroplated Cu Cu-CCC failure

*Samples were cured either for 24 hours at room temperature or 6 hr at 62 °C; no difference in lap-shear strengths was noted. The first two sets of data are reference samples.

The first two data sets demonstrated that good adhesion could be obtained by joining aluminum samples with Loctite 334. This adhesive is a toughened methacrylate resin with some bismaleimide oligomer. With data set 3, failure was similar to that observed with the soldering process: the primary mode of failure was interlaminar carbon-carbon separation. The breaking strengths were similar to values obtained for solder compounds. Interesting, however, was that failure mode and breaking strengths were the same when the copper-coated aluminum was replaced with an uncoated piece of CCC: the bond to the uncoated CCC remained intact. Adhesively bonded CCC-CCC specimens (data set 5) were slightly stronger than any of the CuCCC samples: adhesive rather than interlaminar failure occurred with these samples. Sections of electroplated Cu to CCC were also bonded to CuAl (data set 6). Electroplating was not expected to give as strong a Cu-CCC bond as would the refractory metal-Cu coating process.^{6,7} As expected (data set 6) the breaking strengths were lower, and very little of the carbon adhered to the copper surface.

The above experiments point to interlaminar failure within the layers of the CCC, rather than failure of the Cu-CCC bond as the major failure mode for all of the CuCCC specimens. (The only exception being the electroplated Cu-CCC samples, Table 2.6). The breaking strengths are consistent with the interlaminar shear strength of 1000 psi (double notch test) reported by the manufacturer⁸. An independent verification of the interlaminar shear strength was made using two different batches of CCC's obtained from the manufacturer: Using a short beam shear test (ASTM D 2344) an average shear strength of 1300 psi was obtained.

2.7 Thermoconductivity Testing

Heat transfer is an important requirement for electronic thermal management (SEM-E) applications.¹¹ Advanced thermal protection materials are also envisioned for a variety of uses on future hypersonic vehicles.¹² For high-performance, light-weight composites, carbon fibers have thermal conductivity properties equivalent to or surpassing copper, aluminum, or beryllium. While fibers impart the primary strength and heat transfer properties, matrix resins play an important role the final determination of thermal management performance of the composites.

Adhesives also provide a key role in the transfer pathway for the thermal mass from the electronics to the heat sink.¹¹ Adhesives should be both thermally and electrically conductive in these applications. As previously mentioned, soldering offered better potential for developing joints with good thermal and electrical conductivity. A number of composite testing labs were contacted to determine the interest and feasibility in obtaining measurements on laminates prepared by the HEEB process. One of the labs contacted, Precision Measurements & Instruments Corp (PMIC)¹³, was testing similar samples for Lockheed-Martin Colorado. A decision was made to have thermal conductivity testing done at PMIC because our results could be compared with Lockheed-Martin samples. Measurements will be made with PMIC's test system based on ASTM standard C-518 guarded heat flux sensor technique performed under vacuum.¹⁴ Lockheed-Martin expressed an interest in our approach to prepare stress-free Al-CCC joints with good thermal-physical properties.¹⁵ Samples have been sent to PMIC for testing, and results should be available within a month.

3. Conclusion

We have shown that a high energy electron beam (HEEB) process can be used to join copper-coated carbon-carbon composites to aluminum. Lap-shear strengths between 500 and 1600 psi were obtained for a series of samples using four different solder compositions. The principal failure mode appears to be interlaminar failure within the carbon-carbon composite, rather than between the copper and the carbon-carbon substrate or at the solder joint. Since the interlaminar shear strength of the carbon-carbon composite is approximately 1000 psi⁶, the copper coating combined with the soldering process produces a joint that is equivalent to the interlaminar strength of the carbon-carbon.

4. Plans for the Next Quarter

During the remainder of the contract, we will continue experimental soldering/brazing of CCC's to aluminum, and high-temperature materials, including CCC's. Soldering experiments will be based primarily on Cu-coated substrates, although other metal surfaces which bond to carbon will also be considered: several suppliers of chemical vapor deposition (CVD) coating have been contacted in this regard. Experiments will be designed to maximize bonding surfaces and lap-shear strengths, and to reduce residual stresses formed in the joining processes. Additional thermal conductivity measurements will be made if needed to determine the suitability of solder joints for electronic thermal management.

A discussion with the supplier of C-CAT carbon composite indicated that an additional heat treatment might prove beneficial to obtaining better adhesion of copper to the carbon surface. Additional carbon plates will be copper coated and soldered to test this theory if time permits.

Mechanical and thermal properties of solder joints prepared with the solder iron and furnace will be compared with solder joints prepared via the EB process. Bonding experiments of CCC's and aluminum using selected thermoset adhesives, both thermally and EB-cured, will be conducted as time permits, and the properties will also be compared with solder joints prepared via the EB process.

No further contact was made with Rohr during this period. General Electric's program to join CCC's to refractory metals is currently not active. Both companies indicated they would get back to us if this was a future need. Contact with Lockheed-Martin will continue, since this looks to be favorable for transitioning the EB process into commercial applications.

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15. Suraj Rawal, Lockheed Martin Denver, CO, private communication, October 1997.

The conclusion that most of the samples fully bonded was determined by inspection of the samples after failure. "Fully bonded" implies that both the upper and lower solder surfaces melted and coalesced to form a solder joint. The exception was the HMP solder, which is the highest melting solder composition used in this study. The upper melting temperature of HMP solder is 301 °C. Since the upper carbon surface temperature recorded for the EB experiments was at least 600 °C, this should have been sufficient to join the surfaces. Inspection of the HMP solder samples revealed that not all of the solder melted; either the EB did not uniformly heat the intended solder joint or the surface temperature measurement is not an accurate indicator of the temperature at the interface. Uniform heating would be especially important for the higher melting solders and braze metals.

The question still remains as to why the present samples are weaker than those reported in the last period. Possibly the higher temperatures weakened the copper-carbon interface. On the other hand, the duration of the present experiments was only a fraction of a second, compared to several seconds previously used. Two additional sets of experiments were run in an attempt to shed light on the failure mechanism. In the first case, samples were soldered using either a soldering iron or an acetylene torch. Results shown in **Table 2.5** indicate that conventional soldering can produce joints equal to or better than the joints prepared by the HEEB process (compare with **Table 2.4** in this report and from the last progress report, reference 5).

Table 2.5 Iron/Torch Soldering and Adhesive Bonding of Cu-Coated CCC to Cu-Coated Aluminum. Lap-Shear Strengths.

Solder or Adhesive	Strength (psi)	Elongation (in)	Comments
K44 40/60	723-1390	0.05-0.15	100% area bonding interlaminar failure
Eutecrod	635-1000	0.05-0.087	Same as above
Oatey SF	990	0.07	Same as above
HMP	825-1260	0.05-0.06	Incomplete Bonding Interlaminar failure

In the second set of experiments, both copper-coated CCC and uncoated CCC specimens were bonded to aluminum and uncoated CCC specimens using a standard structural adhesive, Loctite 334. Electroplated Cu*CCC was also used. The results are shown in **Table 2.6**.

Table 2.6 Lap-Shear Strengths of Adhesive Bonded Specimens Using Loctite 334*

Data Set	Specimen	Strength (psi)	Elongation (in)	Comments
1	Al to Al	> 1000	0.1	Did not break
2	CuAl to CuAl	> 1000	0.1	Did not break
3	CuCCC to CuAl	536-1200	0.09-0.2	Interlaminar failure
4	CuCCC to CCC	758-890	0.12-0.14	Interlaminar failure CuCCC plate
5	CCC to CCC	1098-1364	0.11-0.14	Adhesive Failure
6	Cu [#] CCC to CuAl	327-385	0.09-0.1	[#] electroplated Cu Cu-CCC failure

*Samples were cured either for 24 hours at room temperature or 6 hr at 62 °C; no difference in lap-shear strengths was noted. The first two sets of data are reference samples.

The first two data sets demonstrated that good adhesion could be obtained by joining aluminum samples with Loctite 334. This adhesive is a toughened methacrylate resin with some bismaleimide oligomer. With data set 3, failure was similar to that observed with the soldering process: the primary mode of failure was interlaminar carbon-carbon separation. The breaking strengths were similar to values obtained for solder compounds. Interesting, however, was that failure mode and breaking strengths were the same when the copper-coated aluminum was replaced with an uncoated piece of CCC: the bond to the uncoated CCC remained intact. Adhesively bonded CCC-CCC specimens (data set 5) were slightly stronger than any of the CuCCC samples: adhesive rather than interlaminar failure occurred with these samples. Sections of electroplated Cu to CCC were also bonded to CuAl (data set 6). Electroplating was not expected to give as strong a Cu-CCC bond as would the refractory metal-Cu coating process.^{6,7} As expected (data set 6) the breaking strengths were lower, and very little of the carbon adhered to the copper surface.

The above experiments point to interlaminar failure within the layers of the CCC, rather than failure of the Cu-CCC bond as the major failure mode for all of the CuCCC specimens. (The only exception being the electroplated Cu-CCC samples, Table 2.6). The breaking strengths are consistent with the interlaminar shear strength of 1000 psi (double notch test) reported by the manufacturer⁸. An independent verification of the interlaminar shear strength was made using two different batches of CCC's obtained from the manufacturer: Using a short beam shear test (ASTM D 2344) an average shear strength of 1300 psi was obtained.

2.7 Thermoconductivity Testing

Heat transfer is an important requirement for electronic thermal management (SEM-E) applications.¹¹ Advanced thermal protection materials are also envisioned for a variety of uses on future hypersonic vehicles.¹² For high-performance, light-weight composites, carbon fibers have thermal conductivity properties equivalent to or surpassing copper, aluminum, or beryllium. While fibers impart the primary strength and heat transfer properties, matrix resins play an important role the final determination of thermal management performance of the composites.

Adhesives also provide a key role in the transfer pathway for the thermal mass from the electronics to the heat sink.¹¹ Adhesives should be both thermally and electrically conductive in these applications. As previously mentioned, soldering offered better potential for developing joints with good thermal and electrical conductivity. A number of composite testing labs were contacted to determine the interest and feasibility in obtaining measurements on laminates prepared by the HEEB process. One of the labs contacted, Precision Measurements & Instruments Corp (PMIC)¹³, was testing similar samples for Lockheed-Martin Colorado. A decision was made to have thermal conductivity testing done at PMIC because our results could be compared with Lockheed-Martin samples. Measurements will be made with PMIC's test system based on ASTM standard C-518 guarded heat flux sensor technique performed under vacuum.¹⁴ Lockheed-Martin expressed an interest in our approach to prepare stress-free Al-CCC joints with good thermal-physical properties.¹⁵ Samples have been sent to PMIC for testing, and results should be available within a month.

3. Conclusion

We have shown that a high energy electron beam (HEEB) process can be used to join copper-coated carbon-carbon composites to aluminum. Lap-shear strengths between 500 and 1600 psi were obtained for a series of samples using four different solder compositions. The principal failure mode appears to be interlaminar failure within the carbon-carbon composite, rather than between the copper and the carbon-carbon substrate or at the solder joint. Since the interlaminar shear strength of the carbon-carbon composite is approximately 1000 psi⁶, the copper coating combined with the soldering process produces a joint that is equivalent to the interlaminar strength of the carbon-carbon.

4. Plans for the Next Quarter

During the remainder of the contract, we will continue experimental soldering/brazing of CCC's to aluminum, and high-temperature materials, including CCC's. Soldering experiments will be based primarily on Cu-coated substrates, although other metal surfaces which bond to carbon will also be considered: several suppliers of chemical vapor deposition (CVD) coating have been contacted in this regard. Experiments will be designed to maximize bonding surfaces and lap-shear strengths, and to reduce residual stresses formed in the joining processes. Additional thermal conductivity measurements will be made if needed to determine the suitability of solder joints for electronic thermal management.

A discussion with the supplier of C-CAT carbon composite indicated that an additional heat treatment might prove beneficial to obtaining better adhesion of copper to the carbon surface. Additional carbon plates will be copper coated and soldered to test this theory if time permits.

Mechanical and thermal properties of solder joints prepared with the solder iron and furnace will be compared with solder joints prepared via the EB process. Bonding experiments of CCC's and aluminum using selected thermoset adhesives, both thermally and EB-cured, will be conducted as time permits, and the properties will also be compared with solder joints prepared via the EB process.

No further contact was made with Rohr during this period. General Electric's program to join CCC's to refractory metals is currently not active. Both companies indicated they would get back to us if this was a future need. Contact with Lockheed-Martin will continue, since this looks to be favorable for transitioning the EB process into commercial applications.

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